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Ion-Assisted Deposition of Tungsten Oxide

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Ion-Assisted Sputtering of Tungsten Oxide Solar-Control Films

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Abstract

Spectrally selective solar control films can greatly reduce solar heat gain from the infrared while admitting a high fraction of visible daylight. Single-crystal tungsten bronzes of general formula M_xWO_3, where M is a metal, can have sharp spectral selectivity, but this property is difficult to obtain in thin films. Reversible electrochromic coloration caused by insertion of alkali metal or hydrogen ions has been extensively studied in WO_3. Polycrystalline films were made by reactive magnetron sputtering of WO_3 together with substrate heating and/or ion bombardment. Bronze forming elements were introduced after deposition either by electrochemical injection of H^+ or Li^+ or by ion implantation of Ag and Cu. During deposition, H_xWO_3 or substoichiometric WO_x could be formed by controlling the sputtering atmosphere. Films treated by ion bombardment had optical properties approaching those of single crystals.

I. Introduction

Spectrally selective coatings with a high visible transmittance and low shading coefficient are usually constructed of antireflected-silver multilayers. Silver is the best choice among the elemental metals for this purpose,[1] but some metallic compounds have a higher degree of intrinsic selectivity as well as greater durability. Many transition-metal nitrides, carbides and oxides have electrical and optical properties similar to transition metals, and a few, like TiN, behave more like noble metals.[2] Some of the rare-earth oxides also have metallic characteristics with very sharp reflectance onsets that are shifted relative to noble metals from the ultraviolet or visible to the near infrared because of low electron densities and mobilities. Some transition-metal oxides intercalated with another metal M, such as the well known tungsten bronzes M_xWO_3, also belong to this category. A variety of these materials have been considered for application to low-emittance coatings.[3,4]

Despite the apparent abundance of viable materials, there are several factors that limit the usefulness of most of them. First, the high level of reflectance often found in bulk crystals of these materials is difficult to achieve in thin films, . Second, the reflection edge does not always fall near the boundary of the visible and solar infrared. Finally, many of the rare earths are very expensive. One material that has been extensively studied because of its electrochromic properties is WO_3, an inexpensive transition metal oxide. With the intercalation of a large fraction of H, Li, Na, or other elements, WO_3 transforms into a metallic bronze closely related to the intrinsically metallic ReO_3.

Goldner et al.[5] produced an electrochromic H_xWO_3 film with infrared reflectance ρ =0.62 at wavelength λ=2.5 μm by sputtering at a substrate temperature between 230-325 °C and they also showed that the Drude free-electron model fit the reflectance data. Svensson and Granqvist[6] examined the theoretical dependence of the optical properties of WO_3 on the physical parameters of this model. Cogan et al.[7] found a limit to ρ of <0.6 for electrochromic $Li_{0.5}WO_3$ at a deposition temperature of 466 °C. Goldner et al.[8] reported Li_xWO_3 with $\rho=0.69$ which they attribute to improved oxygen stoichiometry. Recently, Arntz, Goldner, et al.[9] produced crystalline electrochromic Li_xWO_3 films with $\rho>0.5$ at temperatures below 100 °C by ion-assisted evaporation.

In this paper we show that ion-assisted sputtering can be used to grow WO_3 films with optical properties near the single-crystal limit at high growth temperature and with enhanced reflectance even at low temperature. Bronzes are formed by both electrochemical means and by ion implantation without consideration for their electrochromic properties.

II. Methods And Results

All coatings were deposited by reactive magnetron sputtering under the general conditions of Table 1. For electrochromic coatings we use different deposition parameters and a special geometry designed to minimize particle bombardment. High ion conductivity and high infrared reflectivity are not mutually exclusive, but a trade-off usually occurs. Optical transmittance and reflectance were measured over the solar spectrum using a Perkin-Elmer Lambda 9 spectroradiometer, and over the midinfrared using a Nicolet PC5 Fourier-transform spectrometer with a CsI extended-range beamsplitter.

Table 1. Deposition Parameters

Target	99.99% W, 50-mm diameter
Target-to-Substrate Distance	70 mm
Substrates	soda-lime glass or fused silica
Substrate Temperature	ambient or 450 C
Total Pressure	20 mTorr
Oxygen Flow Rate	10% O_2

The usual method for electrochemically injecting bronze-forming species requires that the substrate be precoated with a transparent conductor. This is neither necessary nor desirable for static solar control coatings. For our purposes, electrochemical injection of charge was achieved without a conducting sublayer by using the method of Pifer and Sichel[10] to create a local potential. Substoichiometric WO_x films and H_xWO_3 films were also deposited by reducing the O_2 flow or adding H_2 to the sputtering atmosphere. Finally, we could also inject various metal species using a miniature high-current ion implanter developed at LBL.[11]

First we deposited WO_3 coatings under conditions that could be recreated in existing production coaters. Ideally, the films would be deposited without deliberate substrate heating, although large moving substrates could conceivably be heated without contact by infrared lamps. Ion-assisted sputtering, however, through the use of unbalanced magnetrons, is a currently available industrial technology, although control of the beam characteristics is difficult. Figure 1 shows that the reflectance of a 1000-A thick film deposited with supplemental ion bombardment at about 100 eV, but without heating, is almost identical to films sputtered at high temperature. [5,7]

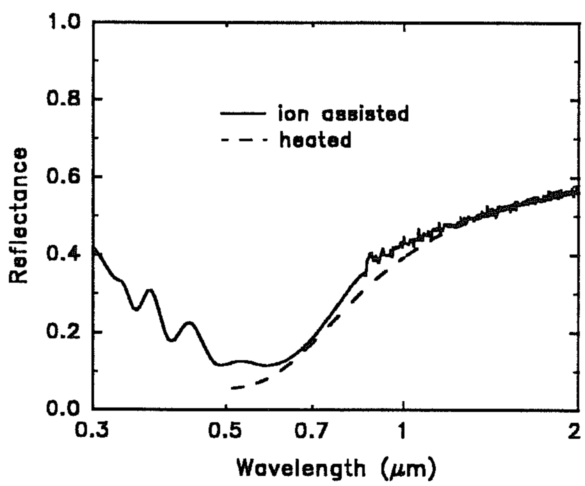

Fig. 1 Spectral reflectance of a H_xWO_3 film deposited by ion-assisted sputtering at room temperature compared to a $Li_{0.5}WO_3$ film sputtered at high temperature.

To approach the ideal (single-crystal) properties as closely as possible we had to use substrate temperatures that are not compatible with current large-scale industrial practice. Using heated substrates alone we found that the infrared reflectance of our films approached an upper limit at about 450 C. Cogan et al.[5] observed a slight downturn in reflectance at 466 C, which was attributed to either a structural phase transformation or oxygen loss. Although we did not see this downturn, we found only a small monotonic increase in reflectance using quartz substrates and even higher temperatures up to 800 C. A combination of moderately high temperature and increased ion flux from a slightly unbalanced magnetron resulted in significantly higher reflectance. Figure 2 shows the optical properties for a 1000-A thick film deposited at 450 C on glass compared to the calculated spectrum of Karlsson and Karlsson[4] which was derived from the optical constants of Owen and Teegarden[12] for a single crystal of $Na_{.522}WO_3$. The two spectra have similar shapes, although the infrared reflectance of our film is lower.

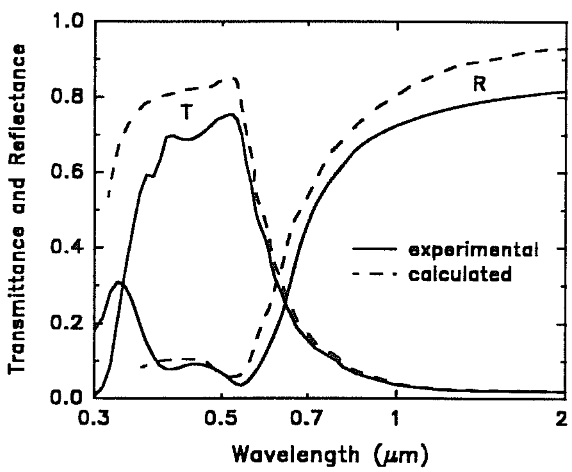

Fig. 2 Spectral transmittance and reflectance of a Ag_xWO_3 film deposited at 450 C using ion-assisted sputtering compared to film properties calculated from single-crystal data from $Na_{.522}WO_3$.

From these properties we can calculate the average visible transmittance T_{vis} and shading coefficient SC using the WINDOW 4.0 program. The SC is a measure of the total solar heat gain from both directly transmitted solar radiation as well as from absorbed radiation that is indirectly transferred. The film of Fig. 2 has $T_{vis}=0.56$, SC=0.38. Figure 3 shows that these properties are comparable to the best silver/dielectric coatings, although it has a blue color. Any transmitted visible light carries a penalty of solar heat so that SC can never equal zero. The "forbidden zone" in the lower right corner of the selectivity diagram thus represents an unattainable ideal. The hemispherical emittance E_h of this coating was calculated to be 0.21 from the measured infrared reflectance. The E_h is rarely measured or reported for electrochromic WO_3 because the electrochromic layer will be hidden by infrared-opaque contacts and glass in an electrochromic device. For static spectrally selective coatings, however, even the moderately low emittance of this coating is sufficient to halve the thermal conductance of a double-glazed window.

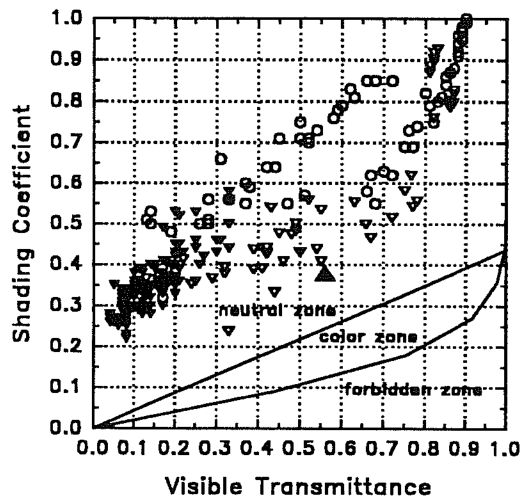

Fig. 3. Selectivity diagram comparing our tungsten oxide coating to commercially available products. O -monolithic glasses, ▲ -WO_3 film, ▼ -durable coatings, and ∇ -nondurable coatings. Ideally, coatings would have properties as close as possible to the "forbidden zone".

III. Conclusions

Single layers of M_xWO_3 show promise as alternatives to silver-based multilayers for spectrally selective coatings. Ion bombardment proved to be at least as effective as substrate heating in crystallizing and enhancing the infrared reflectivity of M_xWO_3 films. High temperature alone was insufficient to achieve optical properties approaching those of single crystals. Dense layers that are not well suited to electrochromic applications were found to have higher reflectivity. Also, nonmobile ion implanted species could be effective bronze formers.

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